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Dehydration of Methyl α-Hydroxyisobutyrate Catalyzed by Zeolites

K. J. Balkus, Jr. and A. K. Khanmamedova

Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75083-0688

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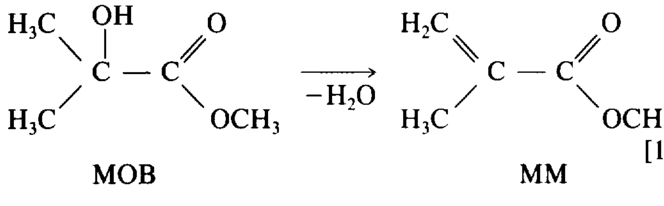
The catalytic dehydration of methyl α-hydroxyisobutyrate over various zeolites in a flow reactor is described. Both NaY and NaX are effective catalysts for the selective conversion of MOB to methyl methacrylate. Modification with K^+ and Cs^+ enhances the activity and selectivity of NaY but renders NaX a less effective catalyst. Acidic zeolites (HY, Beta, GdNaX, SmNaY, fluorinated SmNaY) were shown to be quite active but poorly selective with catalyst deactivation resulting from coke formation.

INTRODUCTION

The dehydration of α- or β-hydroxycarboxylic acids and esters as well as the α- or β-alkoxy analogues to give the corresponding unsaturated acrylate derivatives is a reaction with great commercial interest. For example, a key step in the Mitsubishi acetone cyanohydrin process to produce methyl methacrylate (MM) (1, 2) involves the dehydration of methyl α-hydroxyisobutyrate (MOB) as shown in Eq. [1]. The dehydration of alcohols is generally an easy transformation. However, in this case the close proximity of the carboxylate group makes selective dehydration a challenge because of potential oxidative decarboxylation to give acetone. Additionally, de-esterification of the carboxylate, esterification of the alcohol, and polymerization of product methacrylate further complicate the reaction.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The patent literature reveals several potential catalysts including silica alumina (1, 3) antimony pentoxide on silica (4). Additionally, X or Y type zeolites in the presence of a group VIII metal such as Ru or Pt have been disclosed as catalysts (5). Zeolites are attractive as catalysts for this reaction because the acidity and basicity as well as shape selectivity can be systematically varied. Additionally, zeolites have already been shown to be active catalysts for the dehydration of certain alcohols (6–15). In particular, the dehydration of isopropanol is often employed as a model reaction to probe catalyst acid/base properties (16) as well as the dehydration of cyclohexanol (17). In general, it appears basic sites favor formation of acetone from isopropanol, while acidic sites lead to propylene (18, 19). A recent NMR study suggests the mechanism of alcohol dehydration include carbocation formation (20). Zeolites, including aluminosilicates and borosilicates of the pentasil type, have been shown to be catalysts for the dehydration of α-hydroxyketones to α, β-unsaturated ketones (21). The activity and selectivity of the borosilicate zeolites can be increased by doping the catalyst with cerium (III). We have shown that NaY zeolites exchanged with samarium (III) and further modified with various loadings of fluorine are effective catalysts for the selective dehydration of methyl butyraldehyde to isoprene (22). In this same study it was shown that H–ZSM-5 was also quite active but poorly selective, suggesting that both acidity and pore structure are important in these reactions. Since zeolite NaX was claimed as an effective catalyst for methacrylate production (5) it would appear that strong acidity may not be necessary. Therefore, we decided to evaluate a series of zeolites that covered a range of acidities and pore sizes. In this paper we report the results for MOB conversion over X, Y, and Beta type zeolites.

METHODS

Zeolite NaY (LZY-52, Si/Al = 2.7) was obtained from Union Carbide. Zeolites NaX (Si/Al = 1.2) and NaA were obtained from Aldrich. Zeolite Beta (Si/Al = 25) was obtained from PQ Corporation. All commercially obtained zeolites were pretreated with a 1 *M* NaCl solution by stirring 2 g of zeolite in 100 ml of salt solution at room temperature for 48 h. The zeolites were separated by suction filtration and washed with deionized (pH ~ 6.5) water until the filtrate tested negative for chloride ions ($AgNO_3$ test). Samples were then dried at 100°C for 18 h.

Zeolite HY was prepared from the NH_4Y (LZY-62)

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by heating under an oxygen stream at 400°C overnight. SmNaY (11.07% Sm by weight) was prepared by treating NaY zeolite (112 g) four times with 500 ml aliquots of a 0.07 M aqueous solution of $SmCl_3$ (Aldrich) at 65°C. The zeolite was stirred with each portion for 3 h. The initial pH was 2.5 which increased to 4 after the first exchange. The last exchange did not result in a solution pH change. The Sm(III)-exchanged zeolite was suction filtered, washed with deionized water until the filtrate tested negative for Cl^- ions, and then dried at 100°C overnight. The fluorination of SmNaY (0.50, 0.85, and 2.05% F by weight) was conducted as previously described (23): NH_4F (13.16, 26.49, and 48.15 mg NH_4F/g SmNaY correspondingly) was deposited in SmY using an incipient wetness technique. The impregnated samples were dried at 100°C for 15 h and then at 450°C overnight.

KNaY (6.00% K by weight) was prepared by stirring 4 g of NaY zeolite in 100 ml of an aqueous 2 *M* KCl solution overnight. The resulting sample was washed with deionized water until the filtrate tested negative for chloride ion, dried at room temperature, and calcined at 450°C for 3 h. CsNaY (2.00% Cs by weight) was obtained by mixing 1 g of zeolite NaY with 100 ml of an aqueous 0.03 *M* CsCl solution at room temperature for 18 h. The sample was suction filtered, washed with deionized water, and dried at 80°C. CsNaY (24.80% Cs by weight) was prepared by stirring 1 g of NaY in 100 ml of an aqueous 0.4 *M* CsCl solution at room temperature for 24 h. Then zeolite was suction filtered, washed with deionized water, and dried overnight at 80°C. KNaX (6.33% K by weight) was prepared by ion exchange of NaX with 2 *M* KCl solution in water. NaX (2 g) was added to 100 ml of the KCl solution and stirred at room temperature for 3 h. The procedure was repeated an additional three times. The sample was then suction filtered, washed with deionized water, and dried at 80°C overnight. CsNaX (2.00% Cs by the weight) was prepared by ion exchange of NaX zeolite with a 0.04 *M* CsCl solution in water. NaX zeolite (1 g) was added to 100 ml of the CsCl solution, stirred at room temperature overnight, suction filtered, washed with deionized water, and dried at 80°C. CsNaX (28.74% Cs by weight) was prepared by stirring of 1 g NaX in 100 ml of a 0.4 *M* aqueous CsCl solution at room temperature overnight. The sample was suction filtered, washed with deionized water, and dried at 80°C.

GdNaX (3.11% Gd by weight) was obtained by stirring 25 g of NaX in an aqueous solution of 2.5 g of $GdCl_3$ in 500 ml of deionized H_2O. The suspension was stirred 24 h at room temperature, suction filtered, washed with deionized water, and dried at 100°C. Gadolinium assays were obtained as previously reported (24). GdNaX (5.92% Gd by weight) was similarily prepared by mixing 25 g of NaX with 2.5 g of $GdCl_3$ in 500 ml of H_2O. The suspension was stirred for 3 h at room temperature. The zeolite was then decanted and a new portion of $GdCl_3$ was added (2.5 g of $GdCl_3$ in 500 ml of deionized water) with stirring for an additional hour. The zeolite was then suction filtered, washed with deionized water, and dried at 100°C. The highest loading GdNaX (11.60% Gd by weight) was achieved by suspending 25 g of NaX in a solution of 2.5 g of $GdCl_3$ in 500 ml of deionized H_2O. The zeolite suspension was stirred for 6 h at room temperature. The zeolite was decanted and a new portion of the $GdCl_3$ solution was added (2.5 g in 400 ml of H_2O). Stirring was continued for 4 h at room temperature. The GdNaX was then suction filtered, washed with deionized water, and dried at 100°C.

All elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). Zeolite samples were also analyzed by infrared spectroscopy and X-ray powder diffraction after modification to ensure that crystallinity was maintained.

The dehydration reactions were conducted in a quartz, flow reactor with a 5 mm ID and length of 200 mm. The tube was packed 0.1 g of zeolite (2–3 mm). Methyl α-hydroxyisobutyrate (0.63 g h^{-1}) and methanol (0.34 g h^{-1}) were preheated in a nitrogen carrier stream (390 ml h^{-1}). The molar ratio of MOB : MeOH : N_2 was 1 : 2 : 3.3 (mol). Products were taken from the downstream using a calibrated sampling loop and analyzed using a Hewlett–Packard model 5700A gas chromatograph with FID detector. Products were separated using a $\frac{1}{8}''$ SS column packed with polyphenylether on chromosorb. The zeolites were activated for 1 h at 400°C in the flow of nitrogen (30 ml min^{-1}) prior to reaction. Conversion of the MOB–MeOH mixture was measured over a 200–400°C temperature range 30 min after the start of the reaction to ensure a stable temperature. Conversion is reported as the mol.% of starting material (MOB) consumed. Selectivity is reported as the mol.% of MM obtained divided by the mol.% of starting material consumed and normalized to 100%. The rate of product formation, *V*, was calculated as the amount (mmol) of product (MM, methacrylic acid (MA), acetone) obtained per hour over 1 m^2 of catalyst surface.

RESULTS AND DISCUSSION

The conversion of methyl α-hydroxyisobutyrate with a cofeed of methanol was measured over a series of zeolite catalysts in a flow reactor between 200 and 400°C. The methanol is necessary to minimize formation of methacrylic acid. Both dimethyl ether and methyl α-methoxyisobutyrate are formed in small amounts as a consequence of the methanol; however, selectivity towards the olefin is improved. Although methacrylic acid is also a dehydration product, which may arise partially from the de-esterification of product methyl methacrylate, the product selectivity is reported only for MM formation.

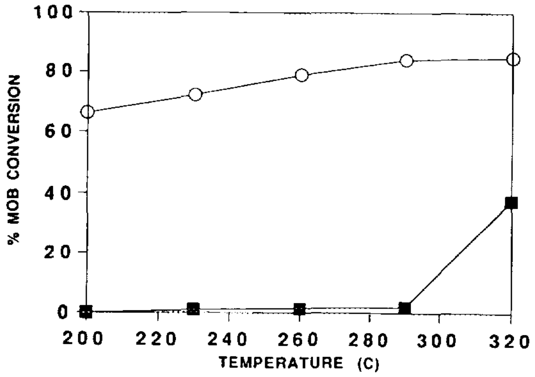


FIG. 1. Plot of MOB conversion versus reactor temperature towards zeolite Beta (○) and zeolite HY (■).

TABLE 1

Results for MOB Dehydration Catalyzed by NaY[a]

	V_{MM}	V_{MA}	$V_{Acetone}$	Conversion	Selectivity
T(°C)	mmol/m^{2}h($\times 10^{-2}$)			mol.%	
200	0.3	0.1	0.0	1.4	21.5
230	2.8	0.2	0.0	8.5	28.3
260	13.9	0.5	0.0	35.2	34.0
290	49.4	1.2	Trace	65.0	65.5
320	61.0	1.2	Trace	72.0	73.1

[a] NaY was activated at 400°C for 1 h in flow of N_2 (30 ml min^{-1}); MOB/MeOH : N_2 = 1 : 2 : 3.3 (mol.); contact time 0.8 s.

Not surprisingly, zeolite NaA was fairly inactive for MOB conversion because of the small pores and little or no acidity. However, HY was also a poor catalyst for this reaction with only some formation of MM and acetone in part because of rapid coke formation. In contrast, zeolite Beta is quite active as shown in Fig. 1. Although both zeolites show evidence of severe coking after a short time on stream, zeolite Beta with the higher Si/Al ratio is more resistent. This coking appears to be a general problem with all the strong acid zeolites tested.

The conversion of MOB over zeolite Beta increases with temperature but selectivity towards MM decreases as shown in Fig. 2. A maximum in selectivity (50%) over this catalyst was observed at 230°C. The HY zeolite showed activity only at high temperature. At 320°C HY produced only trace amounts of MM with predominant formation of acetone (18%). Interestingly, the formation of acetone (~15–18%) over zeolite Beta was fairly unchanged with temperature.

In contrast to HY, zeolite NaY exhibited high activity and selectivity as shown in Table 1. Both selectivity and conversion towards methyl methacrylate increase with temperature. However, acetone begins to appear at 290°C. The disparity in rate of MM produced and the selectivity towards MM in the detectable products arises from polymerization of the olefin, which was apparent from a slight yellowing of the catalysts after several hours on stream.

Recently it was shown that fluorinated SmNaY zeolites exhibit increased activity for the dehydration of methylbutylaldehyde to isoprene (21). The acid sites for NaY zeolite exchanged with Sm^{3+} have been well characterized (25), so these samples were evaluated for the reaction of MOB dehydration as shown in Fig. 3. The exchange of NaY with Sm^{3+} improves the conversion as expected from a stronger acid zeolite but the selectivity towards MM is relatively unaffected. Fluorination of SmNaY appears to have little influence on this reaction.

Since water is a product in this reaction the rate of dehydration and water desorption is important. This will determine the equilibrium concentration of surface hydroxyl groups. In order to evaluate the effects of water on this reaction, a feed stream with the molar ratio

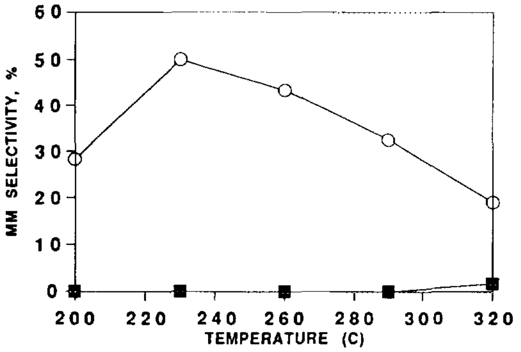


FIG. 2. Plot of selectivity of MM formation versus reactor temperature towards zeolite Beta (○) and zeolite HY (■).

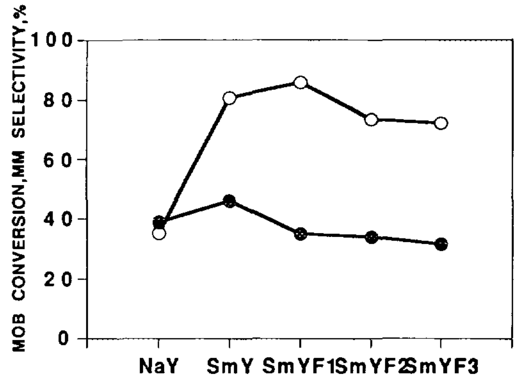


FIG. 3. MOB conversion at 260°C (○) and MM selectivity (●) (at 40% MOB conversion) over zeolites with feed stream MOB : MeOH : N_2 = 1 : 2 : 3.3.

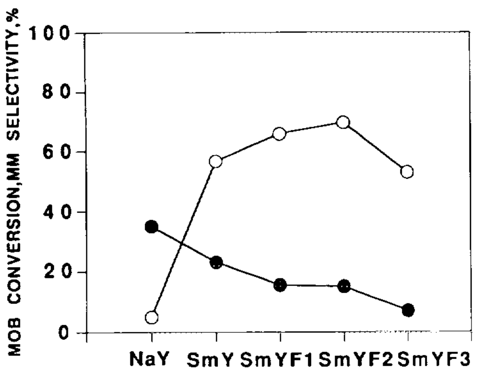
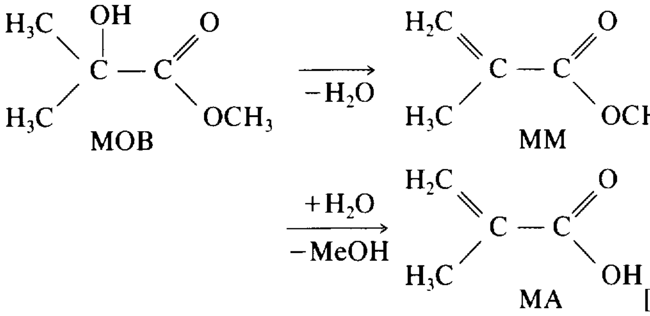


FIG. 4. MOB conversion at 260°C (○) and MM selectivity (●) (at 40% MOB conversion) for a feed having the molar ratio MOB : H_2O : N_2 = 1 : 2 : 3.3.

MOB : H_2O : N_2 = 1 : 2 : 3.3 was tested over NaY, SmNaY, and the fluorinated SmNaY samples as shown in Fig. 4. For all samples water depresses MOB conversion and selectivity towards MM formation. The decreasing of MOB conversion may be explained by competitive adsorption of water. The loss in selectivity is largely a consequence of de-esterification and formation of methacrylic acid as shown in Eq. [2]. Methanol was detected as a product after addition of water to the feed.



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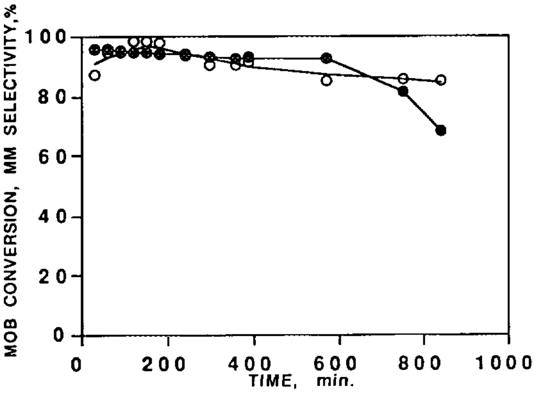

FIG. 5. The effect of time on stream for a NaX activated under N_2 prior to reaction. (●) MOB conversion, (○) MM selectivity.

TABLE 2

Results for MOB Dehydration Catalyzed by NaX

	V_{MM}	V_{MA}	$V_{Acetone}$	Conversion	Selectivity
T(°C)	mmol/m²h(× 10^{-2})			mol.%	
	NaX activated under N_2 for 1 h				
230	8.3	0.0	0.0	10.3	61.2
260	26.6	Trace	0.0	30.0	67.5
290	83.1	0.1	Trace	75.0	83.7
320	100.4	0.1	Trace	86.6	87.6
	NaX activated in air for 1 h				
230	1.6	0.0	0.0	4.5	24.4
260	6.5	0.1	0.0	12.6	40.0
290	56.9	0.6	0.0	62.4	68.8
320	92.1	0.1	0.0	82.3	84.6
	NaX activated under N_2 for 2 h				
230	8.1	Trace	0.0	10.0	61.0
260	59.3	1.1	0.0	65.8	68.1
290	99.3	0.4	0.0	95.1	78.9
320	89.3	0.4	1.2	96.6	69.9
	NaX activated for 2 h (MOB/MeOH) : N_2 = ($\frac{1}{2}$: 1.8)				
230	7.9	0.0	0.0	7.0	85.7
260	82.0	1.6	0.0	82.1	75.5
290	94.8	0.4	1.0	94.4	76.0
320	92.1	0.4	1.3	98.3	70.8
	NaX activated under N_2 for 1 h (contact time 6 s)				
230	35.1	0.9	0.0	53.8	49.3
260	53.7	0.3	1.1	92.9	43.7

Since increasing the relative acidity did not improve selectivity we decided to examine the activity of the more basic NaX zeolite. Figure 5 indicates high conversions and selectivity towards MM over several hours. Eventually, polymers are formed in the reactor reducing the conversion. Based on these results, data recorded after 30 min appear representative of the catalyst activity.

Since NaX appeared to be such a promising catalyst, we examined the effects of varying the catalyst pretreatment conditions. Our results with NaY are similar to those claimed by Mitsubishi, where a K^+-exchanged NaY exhibited 100% conversion with 59% selectivity at 400°C (26). Under the same conditions NaX is slightly more active as shown in Table 2, where at 320°C the conversion was ~87% versus 72% for NaY. The selectivity towards MM also improved to ~88% with the lower catalyst Si/Al ratio. Since water is expected to affect the dehydration reaction as well as de-esterification conditions the zeolites were heated prior to reaction. Under standard conditions the zeolite was activated at 400°C in the reactor under a flow of N_2 for 1 h. If the zeolite is heated under static dry air for 1 h, then both the activity and selectivity is reduced, where apparently the flow is more effective at removing water. The formation of methacrylic acid is expected to increase in the presence of water which arises from the

TABLE 3

Results for MOB Dehydration Catalyzed by NaY Modified with K^+ and Cs^+

	V_{MM}	V_{MA}	$V_{Acetone}$	Conversion	Selectivity
T(°C)	mmol/m^{2}h($\times 10^{-2}$)			mol.%	
		KNaY (6.00% K by wt)			
230	5.1	0.0	0.0	5.0	—
260	9.2	0.4	0.0	11.6	63.8
290	45.0	1.7	0.0	47.1	77.1
320	98.1	1.2	0.0	92.1	85.9
350	95.3	0.3	0.0	93.3	82.4
		CsNaY (2.00% Cs by wt)			
230	5.4	tr.	0.0	4.0	—
260	22.9	1.3	0.0	22.1	68.8
290	86.4	2.7	0.0	77.0	74.5
320	107.1	0.3	0.0	89.5	79.4
350	104.4	0.1	0.0	92.5	74.9
		CsNaY (24.80% Cs by wt)			
200	0.9	0.0	0.0	1.2	45.8
230	2.7	0.1	0.0	3.2	48.1
260	39.8	1.1	Trace	37.5	57.1
290	67.9	0.6	Trace	55.0	67.6
320	36.7	0.2	Trace	28.0	71.7

dehydration of MOB or incomplete desorption of intrazeolite water during activation. Since the formation of MM is reduced and there is a slight increase in MA product after activation, one might conclude the initial zeolite dehydration is not as effective in air as under N_2 flow. Interestingly, there was no acetone formation observed when the catalyst was heated in air. If the NaX is activated longer (2 h) under a flow of N_2, then the activity improves, especially at the lower temperatures (230–290°C). However, the water produced from MOB dehydration at the lower temperatures is adsorbed by the zeolite leading to increased methacrylic acid formation. At 320°C the selectivity is reduced and acetone begins to appear as a product. In an effort to overcome the zeolite adsorption of by-product water at the lower temperatures, the amount of MOB/MeOH reactant mixture in the stream was doubled (Table 2) with a slight increase in contact time (~1.0 s). Both the activity and selectivity were improved, which is consistent with better displacement of water; however, both MA and acetone were produced at >290°C. The best conversion (>98%) was observed at 320°C under these conditions but the selectivity was only ~71%. These results may also be a consequence of increased MOB concentration and by-product water. If one now goes back to the standard activation conditions (N_2, 1 h) and increases the contact time from 0.8 to 6 s the activity dramatically improves at the lower temperatures but the selectivity is poor. So it would appear the most favorable conditions would be when both initial zeolitic water and by-product water are removed quickly from the system.

The better activity and selectivity of the NaX catalyst compared with NaY suggest that a more basic zeolite would favor the transformation of MOB to MM. Therefore, NaY and NaX were ion exchanged with K^+ and Cs^+ in order to generate more basic zeolites. The results for dehydration of MOB over NaY and NaX zeolites modified with K^+ and Cs^+ ions are presented in Tables 3 and 4. A comparison of the results in Table 1 for NaY with those after partial exchange of the zeolite with K^+ (Table 3) indicates a significant improvement in the conversion of MOB as well as enhanced selectivity towards methyl methacrylate. In particular, the selectivity for MM at the lower temperatures is nearly doubled. The higher activity does not significantly increase the formation of MA. Additionally, there was no detectable acetone formed. The NaY catalyst modified with a low (2.00%) and high loading (24.80%) of Cs^+ behaved quite differently. A small amount of Cs^+ enhances the MOB conversion and selectivity but not to the extent of that observed with K^+ exchange. A further increase in Cs^+ loading reduces the activity below that of NaY. The selectivity is better at the lower temperatures and comparable to NaY at > 290°C. However, trace amounts of acetone appear over this catalyst >260°C. NaX exchanged with K^+ was surprisingly less reactive than the unmodified zeolite as shown in Table 4. Likewise, the Cs^+-exchanged NaX zeolites were less active and

TABLE 4

Results for MOB Dehydration Catalyzed by NaX Modified with K^+ and Cs^+

	V_{MM}	V_{MA}	$V_{Acetone}$	Conversion	Selectivity
T(°C)	mmol/m^{2}h($\times 10^{-2}$)			mol.%	
		KNaX (6.30% K by wt)			
230	4.1	Trace	0.0	3.4	—
260	9.0	0.1	0.0	10.0	50.0
290	18.2	0.4	0.0	17.0	59.7
320	23.1	0.4	0.0	9.2	66.5
350	11.5	0.1	0.0	14.6	43.8
		CsNaX (2.00% Cs by wt)			
230	2.9	0.0	0.0	2.0	—
260	19.1	0.6	0.0	13.0	78.7
290	51.1	0.7	0.0	36.8	79.9
320	103.5	0.8	0.0	86.9	68.6
350	77.6	0.3	0.0	77.8	57.5
		CsNaX (28.70% Cs by wt)			
230	1.0	0.0	0.0	<1.0	—
260	2.1	0.0	0.0	1.0	—
290	5.2	Trace	0.0	3.0	—
320	13.7	0.4	0.0	9.3	70.9
350	20.7	0.3	0.0	12.0	83.3

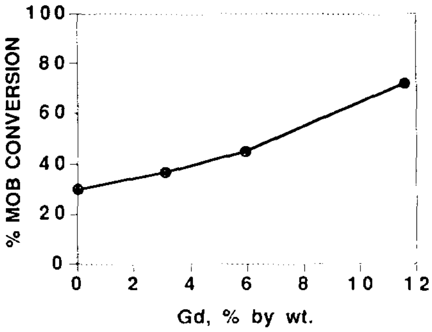

FIG. 6. Plot of MOB conversion versus Gd(III) content in NaX at 260°C.

selective with the high loading of Cs^+ resulting in very poor conversions. It would appear that very basic zeolites are generally poorer catalysts for MOB dehydration. However, the more acidic NaY seems to benefit from modification with heavier alkaline metal ions.

The modification of NaX with acidic metal ions was expected to improve the activity of the zeolite catalysts towards MOB dehydration. Figure 6 shows a plot of MOB conversion at 290°C as a function of gadolinium (III) loading for ion-exchanged NaX. The presence of Gd(III) clearly enhances the activity; however, the selectivity is reduced.

Figure 7 shows a plot of selectivity for MM at a fixed MOB conversion of 40% as a function of Gd(III) loading in NaX. The decrease in selectivity reflects an increase in coking as well as the amount of trace products. The formation of methacrylic acid is somewhat suppressed in the GdNaX zeolites, indicating less free water. Acetone (~3%) was observed only at 320°C. In contrast to NaX, the ion exchange of NaY with Gd(III) dramatically increased the production of acetone to as much as ~20% of the products. The overall conversion and selectivity at <260°C was enhanced but coking becomes a problem.

Trace products. In addition to acetone and methacrylic acid there were several trace products that became obvious from reactions over the strong acid zeolites. It was not surprising that dimethyl ether was observed considering the temperature and acidity of the zeolites. However, dealkylation products, including methyl lactate, lactic acid, methyl acrylate, and acrylic acid, were also detected. Lactic acid (LA) was the most abundant trace product detected with as much as 16 mole % generated by GdNaY. Even NaX produced a small amount of LA. In contrast to a claim of 100% methyl lactate conversion to methyl acrylate over modified NaX (4), we observed only minimal activity. However, MM was detected as a trace product, indicating alkylation reactions can occur as well. Assuming, the alkyl/dealkylation process involves Brönsted sites, we studied the effects of treating NaX with trimethylphosphine (TMP) which is known to bind to these sites. One gram of NaX was treated with 0.02 ml of TMP and calcined at 450°C under O_2 flow overnight. The dehydration of MOB over this catalyst resulted in a conversion of >97% and a selectivity of 93%. Most importantly, there was no detectable LA or acetone. These results underscore how complex this dehydration reaction can be. Nevertheless, it would appear that with careful fine tuning a fairly selective catalyst can be achieved.

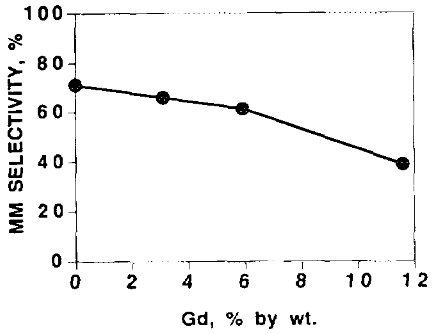

FIG. 7. Plot of MM selectivity at 40% MOB conversion as a function of Gd(III) loading in NaX.

CONCLUSION

The commercially important dehydration of methyl α-hydroxyisobutyrate has been catalyzed by zeolites NaY and NaX. The weakly acidic zeolites favor the formation of methyl methacrylate, while more acidic zeolites (HY, Beta, GdNaY) result in coking and an increase in byproducts. It would appear that temperatures >300°C are preferred in order to remove product water. The NaX catalysts exhibit only a small decrease in activity after several days on stream. However, the stability needs to be evaluated further. It is not clear whether the zeolite structure plays a significant role in this reaction or just the nature of the surface. Work in progress will hopefully address some of these structure/reactivity relationships.

ACKNOWLEDGMENTS

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REFERENCES

1. Aoyama, T., Kida, K., and Uchiyama, T., U.S. Patent 4,613,684 (1986).
2. Higuchi, H., Kida, K., and Ebata, S., Eur. Patent 406,676 (1991).
3. Watanabe, K., Hosaka, N., and Tadokoro, S., Jap. Patent 03,255,053 (1991).
4. Kida, K., Ebata, S., and Yamamoto, Y., Eur. Patent 265,964 (1986).
5. Naito, S., Kouzai, T., and Ikeda, R., Eur. Patent 265,964 (1988).

6. Jacobs, J. M., Jacobs, P. A., Uytterhoeven, J. B., Eur. Patent 175, 399 (1986).
7. Aoki, Y., Tashiro, M., Takahashi, T., Takigawa, A., Maeda, K., Tago, I., and Yoshida, M., Jap. Patent 61 72,727 (1986).
8. Young, L. B., U. S. Patent 4,461,730 (1984).
9. Young, L. B., U. S. Patent 4,461,729 (1984).
10. Yue, P. L., and Olaofe, O., *Chem. Eng. Res. Des.* **62,** 81 (1984).
11. Paukshtis, E. A., Jiratova, K., Soltanov, R. I., Yurchenko, E. N., and Beranek, L., *Collect. Czech. Chem. Commun.* **50,** 643 (1985).
12. Molnar, A., Bucsi, I., and Bartok, M., *Acta Phys. Chem.* **31,** 571 (1985).
13. Malashevich, L. N., and Pismennaya, A. V., *Neftekhimiya* **24,** 664 (1984).
14. Musaev, M. R., Dadashev, B. A., and Mirzoeva, K. G., *Azerb. Khim. Zh.* **6,** 30 (1983).
15. Union Carbide Corp., *Res. Discl.* **264,** 222 (1986).
16. Krylov, O. V., *in* "Catalysis by Non-Metals," p. 118. Academic Press, New York, 1970.
17. Karge, H. G., Kosters H., and Wada, Y., *in* "Proceedings of the 6th International Zeolite Conference, Reno, NV, 1983," p. 466. Butterworth, Guilford, 1984.
18. Hathaway, P. E., and Davis, M. E., *J. Catal.* **116,** 263 (1989); *J. Catal.* **116,** 279 (1989).
19. Frilette, V. J., and Munns, G. W., Jr., *J. Catal.* **4,** 504 (1965).
20. Stepanov, A. G., Zamaraev, K. I., and Thomas, J. M., *Catal. Lett.* **13,** 407 (1992).
21. Hoelderich, W., Schneider, K., and Hupfer, L., Ger. Offen. DE 3,632,530 (1988).
22. Balkus, K. J., Jr., Nowinska, K., and Kowalak, S., *Catal. Lett.* **9,** 145 (1991).
23. Kowalak, S., Pawlowska, M., and Balkus, K. J., Jr., *Collect. Czech. Chem. Commun.* **57,** 781 (1992).
24. Bresinska, I., Balkus, K. J., Jr., and Kowalak, S., *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **38,** 494 (1993).
25. Kowalak, S., Laniecki, M., Khanmamedova, A. K., and Balkus, K. J., Jr., *Catal. Lett.* **24,** 257 (1994).
26. Watanabe, K., Hosaka, N., and Tadokoro, S., Jap. Patent 03,206,066 (1991).